Supporting Information

Rapid, Localized and Athermal Shape Memory Performance Triggered by Photoswitchable Glass Transition Temperature

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Experimental details

Figure S1. Synthetic routes for C11AB6C.

Synthesis of A1. A1 was synthesized according to the literature.  

Synthesis of A2. A1 (4.8 g, 20 mmol) and 11-bromoundecan-1-ol (5.5 g, 22 mmol) and potassium carbonate (5.5 g, 40 mmol) were added into 100 mL flask and dissolved by 40 mL DMF. Then, the mixture was heated at 120 °C for 4 hours and cooled to room temperature. The reaction mixture was extracted by saturated sodium hydroxide solution for 3 times. The crude product A2 was obtained by concentrating the organic phase under vacuum (6.2 g).

Synthesis of A3. A2 (3.0 g, 7.3 mmol), 1,6-hexanediol (1.2 g, 10 mmol) and 4-dimethylaminopyridine (DMAP, 0.5 g, 0.4 mmol) were added into 500 mL flask and dissolved by 150 mL dichloromethane. Then, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 4.5 g, 20 mmol) in 60 mL dichloromethane was added dropwise into the mixture. After stirring at room temperature for 24 hours, the mixture was filtrated to remove the precipitates. The orange solid A3 was obtained by column chromatography with silica gel using dichloromethane (2.7 g, 5.3 mmol, 72%).

Synthesis of C11AB6C. A3 (1.03 g, 2 mmol), 4-(cyclooct-4-en-1-yloxy)-4-oxobutanoic acid (1.13 g, 5 mmol) and 4-dimethylaminopyridine (DMAP, 0.24 g, 0.2 mmol) were added into 250 mL flask and dissolved by 100 mL dichloromethane. Then, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 2.25 g, 10 mmol) in 30 mL dichloromethane was added dropwise into the mixture. After stirring at room temperature for 24 hours, the mixture was filtrated to remove the precipitates. The orange solid C11AB6C was obtained by column chromatography with silica gel using dichloromethane (0.98 g, 1.26 mmol, 63%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.22 -
8.12 (m, 1H), 7.98 - 7.87 (m, 2H), 7.04 - 6.99 (m, 1H), 5.76 - 5.57 (m, 2H), 4.85 (td, J = 9.3, 4.3 Hz, 1H), 4.35 (t, J = 6.6 Hz, 1H), 4.13 - 4.03 (m, 3H), 2.63 - 2.54 (m, 4H).

Figure S2. $^1$H NMR of the crosslinker C11AB6C.

a) Exchange reaction

Figure S3. Various APN actuators prepared by molding method via transesterification reaction. (a) Schematic illustration of the reversible transesterification reaction. (b) Diverse 2D and 3D samples prepared by moulding method. I: snowflake, II: flower, III: spiral shape, IV: tubular shape.

Figure S4. The preparation of the cis-form APN. The trans-form APN was swelled in CH$_2$Cl$_2$ (10 mL) and then was exposed to UV light (365 nm, 40 mW cm$^{-2}$) for 30 minutes. The CH$_2$Cl$_2$ was then removed by a rotary evaporator to obtained the cis-form APN.$^{33}$
**Figure S5.** The evaluation of photothermal effect upon UV light. (a) The temperature measurement of the APN film in the initial state and the irradiated state. (b) Temperature changes of the APN film upon exposure to UV light with different intensities as a function of the irradiation time.

**Figure S6.** Photoinduced reconfiguration of surface pattern. (a) Schematic illustration of shape memory process of surface pattern. (b) A raised pattern was constructed with the APN using lithography. The pattern was pressed into flat after exposure to UV light and fixed by irradiation of visible light, that is, the temporary shape. At last, the raised pattern letter was recovered by UV illumination. Bottom: the shape memory process of raised pattern letter “F”.

**Figure S7.** Shape recovery of the APN sample in the presence of a load. The actuation of the APN sample is not limited to an unloaded state. We prepared a sample with a permanent arched shape, and it was programmed to a temporary flat shape. During the
recovery from flat shape to arched shape, the sample lifted up a load 50 times heavier than the weight of the actuator.

**Figure S8.** Quantitative shape memory cycle to demonstrate the thermo-induced shape memory effect.

**Supporting Movie captions**

**Movie S1.** The shape recovery of the cosmos flower: from a close state to an open state. When the temporary closed flower is placed under a UV light, the cosmos flower recover to initial state during illumination.

**Movie S2.** The Localized shape recovery of the artificial mimosa induced by the UV light spot. The leaves of mimosa underwent rapid shape recovery from open to close state separately as the movement of UV light spot.

**Movie S3.** The programmable shape recovery of the Zigzag strip. The zigzag strip stepwise recovered to a straight strip by programmed illumination of UV light.

**Movie S4.** The shape recovery of the APN sample in the presence of a load. During the recovery from flat shape to arched shape, the sample lifted up a load 50 times heavier than the weight of the actuator due to the geometry difference.

**References**

